



# Use of competitive kinetics for the understanding of deep hydrodesulfurization and sulfide catalysts behavior

Vrinat Michel <sup>\*</sup>, Laurenti Dorothée, Geantet Christophe

*Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS-Université Lyon 1, 2 Av. A. Einstein, 69626 Villeurbanne Cedex, France*

## ARTICLE INFO

### Article history:

Received 25 October 2011

Received in revised form 28 February 2012

Accepted 1 March 2012

Available online 23 March 2012

### Keywords:

Kinetics

Hydrodesulfurization

Sulfide catalysts

Support effect

Rhenium sulfide

## ABSTRACT

Drastic regulations concerning sulfur content in fuels has lead to and still imply numerous researches on hydrotreating reactions and hydrodesulfurization catalysts. The objective of this paper was to illustrate how, besides physicochemical characterization techniques, the kinetics could be also a useful and precious tool for the understanding of the reactions involved and of the catalysts used in this process. That was illustrated by application of competitive kinetics to the comprehension of the transformation of sulfur refractory compounds, of the  $H_2S$  partial pressure effect on the activity of transition metal sulfides, and to the understanding of support effect for rhenium sulfide based catalysts.

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## 1. Introduction

The environmental regulations have forced the oil industry to reduce the sulfur content in gas oil and gasoline which nowadays should contain less than 10 ppm of sulfur for the European market. Such a sulfur reduction has implied a great research effort on hydrotreating (HDT) catalysts in the last decades and many approaches to prepare more active catalysts by varying the preparation method, changing the active component, using alternative supports, organic or inorganic dopants, or combinations of those have been considered.

As regard to the nature of the active phase, following the first papers of Pecoraro and Chianelli [1] and Lacroix et al. [2], dealing with the evolution of catalytic properties of transition metal sulfides with their position in the periodic table, many works on ruthenium, rhenium, vanadium, iridium and ternary sulfides have been published and recently reviewed respectively by de Los Reyes [3], Blanchard et al. [4], Gil Llambias et al. [5], Hubault [6], Vit [7], Afanasiev and Bezverkhyy [8]. Support effect in hydrotreating has not been less studied and several reviews summarized and discussed variations of catalytic activities due to the nature of the support such as alumina, titania, zirconia, zeolites and carbon [9–11].

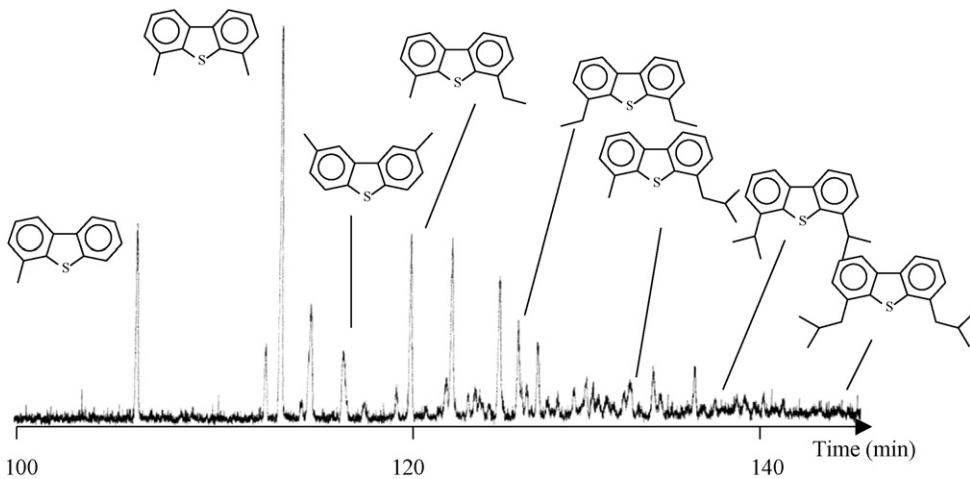
However, if progress obtained on the HDS process was partly coming from the attention given to the development of new catalysts, and particularly to the preparation and activation steps of these solids, it must also be attributed to a better knowledge of the solids and of the reactions involved during hydrotreatment.

Better characterizations of the sulfide catalysts have been obtained thanks to the development of techniques as XPS [12–14], EXAFS [15], HRTEM [16,17] and recently STM [18]. The understanding of the properties of transition metal sulfides has been also deeply improved by using theoretical approach based on density functional theory (DFT) as illustrated in recent reviews by Raybaud [19] or Paul et al. [20] for mixed Co(Ni)MoS active phases. Moreover, thermodynamical calculations clearly demonstrated that the sulfur stoichiometry of these catalysts is deeply dependant on the temperature and on the gas phase surrounding the solid, leading to a great interest in the characterization of these solids under working conditions. That could be performed by *in situ* techniques such as *in situ* XAS, recently reviewed by Geantet and Millet [21], or by IR spectroscopy of CO adsorption as illustrated in the numerous works of Maugé and coworkers [see 22 and references therein].

However, despite the great benefit of these techniques in the understanding of the catalysts, we should not forget that the catalytic reaction itself is certainly also the best way to characterize the catalyst, and the objective of this paper is to demonstrate how (even if unfortunately less and less applied in the laboratories), kinetics was and could still be a useful tool in the understanding of deep hydrodesulfurization (or hydrotreatments) and of sulfide catalysts behavior. That will be particularly illustrated by the study of kinetic parameters in competitive reactions for the transformation

\* Corresponding author. Tel.: +33 04 72 44 53 23.

E-mail address: [michel.vrinat@ircelyon.univ-lyon1.fr](mailto:michel.vrinat@ircelyon.univ-lyon1.fr) (V. Michel).



**Fig. 1.** Gas chromatography (Sievers detection) of a desulfurized gas oil (580 ppm sulfur): identification of some refractory compounds.

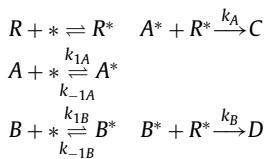
From Ref. [27].

of refractory sulfur compounds in hydrotreating, for the understanding of  $\text{H}_2\text{S}$  effect over transition metal sulfides (TMS), and for the comprehension of support effect with  $\text{ReS}_2$  based catalysts.

## 2. Formalism of competitive kinetics

In competitive kinetics, two compounds  $A$  and  $B$  compete for adsorption on the same sites and  $R$  is the common reactant in the transformation of  $A$  and  $B$ .

The reactions can be schematized as follows:



where the components with asterisk (i.e.,  $A^*$ ) correspond to the adsorbed species,  $k_{1i}$  and  $k_{-1i}$  represent the rate constant of adsorption and desorption respectively of component  $i$  and  $k_i$  the rate constant of the surface reaction of component  $i$ .

At the stationary state of  $A^*$  the balance between the formation and the disappearance of this species could be expressed by:

$$k_{1A}[A].[*] = k_{-1A}[A^*] + k_A[A^*].[R^*] \quad (1)$$

the formation rate of  $C$  is

$$v_C = k_A.[A^*].[R^*] \quad (2)$$

where  $[A^*]$  can be expressed by

$$[A^*] = \frac{k_{1A} \cdot [A] \cdot [*]}{k_{-1A} + k_A \cdot [R^*]} \quad (3)$$

In this expression,  $[i]$  represents the concentration of component  $i$  after a known reaction time,  $[*]$  is the concentration of free active sites (unoccupied sites available for adsorption) at the surface, and  $[R^*]$  is the concentration of the common reactant adsorbed on the catalyst surface.

Similarly,  $[B^*]$  can be expressed by

$$[B^*] = \frac{k_{1B} \cdot [B] \cdot [*]}{k_{-1B} + k_B \cdot [R^*]} \quad (4)$$

If  $[R^*]$  is the same in both expressions, which means that the same species of the common reactant are involved in the transformation of  $A$  and  $B$ , then the ratio is expressed by

$$\frac{v_C}{v_D} = \frac{d[A]}{d[B]} = \left( \frac{k_A \cdot k_{1A} \cdot [A]}{k_B \cdot k_{1B} \cdot [B]} \right) \cdot \left( \frac{k_{-1B} + k_B \cdot [R^*]}{k_{-1A} + k_A \cdot [R^*]} \right). \quad (5)$$

By integration of this equation, the ratio of transformation rates of the molecules  $A$  and  $B$ , named the *reactivity ratio*  $R_{A/B}$ , can be obtained:

$$\frac{\log[A]/[A_0]}{\log[B]/[B_0]} = \frac{k_A \cdot k_{1A}}{k_B \cdot k_{1B}} \cdot \left( \frac{k_{-1B} + k_B \cdot [R^*]}{k_{-1A} + k_A \cdot [R^*]} \right) = R_{A/B} \quad (6)$$

The ratio  $R_{A/B}$  at a given temperature does not depend on the initial composition of the mixture and on the extent of conversion. At relatively low concentration of  $R$ , the surface reaction is the rate-determining step and  $R_{A/B}$  can be expressed as a function of adsorption equilibrium constants and rate constants.

$$R_{A/B} = \frac{k_A \cdot K_A}{k_B \cdot K_B} \quad (7)$$

with

$$k_i = \frac{k_{1i}}{k_{-1i}} \quad (8)$$

representing the adsorption equilibrium constant of compound  $i$  at the surface.

Therefore, a comparison of the  $R$  values with the rate  $s$  ratio  $k_A/k_B$ , calculated from the transformation of each product in separate experiments (performed in conditions of order of reaction relative to the reactant equal to zero), enables the determination of the ratio  $K_A/K_B$  of the adsorption equilibrium constants.

Such formalism has been applied for hydrogenation and hydrodesulfurization reactions in which the common reactant was hydrogen, and examples of understanding of reactions mechanisms and of catalysts behavior using this approach, are given below.

## 3. Application of competitive kinetics for the understanding of refractory sulfur compounds transformation.

Conventional catalytic hydrotreating processes have been used for many years to remove sulfur from distillates containing 1 to 2 wt.% of sulfur. By using these processes, the so-called “easy sulfur” compounds including non-aromatic sulfur, thiophenes, and benzothiophenes are fastly removed. However, a considerable amount

**Table 1**

Rates and selectivities for the transformation of the various alkylbenzothiophenes at 573 K.

	Initial transformation rate ( $10^{-8}$ mol g $^{-1}$ s $^{-1}$ )	S(BP) %	S(CHB) %	S(HN) %	HDS rate ( $10^{-8}$ mol g $^{-1}$ s $^{-1}$ )	Hydrogenation rate ( $10^{-8}$ mol g $^{-1}$ s $^{-1}$ )
DBT	180	87	6	7	157	23
4-MDBT	57	43	27	30	24	33
4,6-DMDBT	30	10	30	60	3	27
2,8-DMDBT	400	93	3	4	372	28

of “hard sulfur” compounds (0.2–0.3 wt.%) is still found in the diesel fraction, after conventional hydrodesulfurization (HDS) [23,24].

It is now well established that deep HDS is hindered mainly by one class of sulfur compounds, the alkyl-dibenzothiophenes (DBT), and more precisely by the  $\beta$ -substituted alkyl-dibenzothiophenes [24–26]. Gas chromatogram of a desulfurized gas oil, obtained using a specific sulfur detector, is given in Fig. 1 and illustrates that point [Ref. 27].

Kinetic investigations of the behavior of such alkyl-dibenzothiophene derivatives under HDS conditions have led to two contradictory proposals. The first hypothesis suggests that the transformation of 4-alkyl- and 4,6-dialkyldibenzothiophenes is limited by the adsorption step; it implies adsorption by the sulfur atom and in this case the alkyl groups sterically hinder adsorption [28,29]. The second proposal assumes that the adsorption of the dibenzothiophene compounds occurs via the  $\pi$ -electrons of the aromatic system. The alkyl groups do not hinder adsorption on the catalyst surface but the elimination step required for the desulfurization reaction is assumed to be hindered by sterical effects.

Considering that the various explanations for the mechanism of DBT transformation are quite contradictory, Meille et al. [30] decided to reexamine the transformation of the refractory alkylbenzothiophenes in order to precise the reaction scheme and to explain the lower reactivity of 4,6-DMDBT. For this purpose, they synthesized the required molecules (2,8-DMDBT, 4-MDBT, 4,6-DMDBT) and compared their reactivities in a batch reactor, on an industrial NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst, in independent and competitive experiments.

### 3.1. Transformation of single molecules

Comparison of reaction rates and selectivities obtained at 573 K for the transformation of DBT, 4-MDBT, 4,6-DMDBT and 2,8-DMDBT are reported in Table 1. The 4,6-DMDBT and the 4-MDBT were found respectively 6 and 3 times less reactive than the DBT. These results confirm that hydrodesulfurization of substituted DBT is inhibited by the presence of methyl groups on the carbon in  $\alpha$  to the sulfur atom. However, in the same conditions, the transformation of 2,8-DMDBT is more than two times faster than that of DBT, thus providing another proof that the loss of reactivity in the case of 4,6-DMDBT was not due to the number of substituents but to their position. It must be pointed out that the calculation of rates according to each pathway clearly shows that the methyl-inhibition in the 4 and 6 positions only affects the DDS pathway leading to the biphenyl type compounds (see Fig. 2), the hydrogenation rates being indeed similar for all the compounds.

### 3.2. Hydrodesulfurization in competitive experiments

Competitive studies were therefore realized in order to understand if the decreasing reactivities of 4-MDBT and 4,6-DMDBT were due to a problem of adsorption on a catalytic site or to difference in the surface reaction rates.

The authors checked that, under our experimental conditions, a pressure of 5 MPa still corresponds to the range of low hydrogen

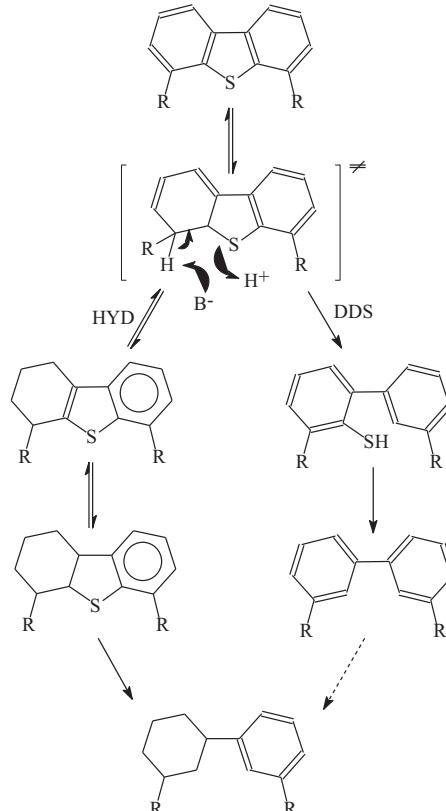


Fig. 2. reaction scheme for HDS of 4,6-DMDBT.

pressure and, thus the formalism of competitive reactions previously described can be applied [30]. Moreover, a separate study of DBT indicated that, under the experimental conditions of the study, the order of reaction relative to DBT was zero. That was also observed for 4,6-DMDBT and was assumed to be true for all other compounds.

Results obtained for competitive experiments between dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT), 2,8-dimethyldibenzothiophene (2,8-DMDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) and reported in Table 2 indicated that the adsorption equilibrium constants of all the dibenzothiophene derivatives are similar and that these compounds are identically adsorbed on the catalyst surface, probably via the  $\pi$ -electrons of the aromatic rings. Thus, the difference of reactivity observed between the alkylbenzothiophenes cannot

**Table 2**

Results of competitive experiments (573 K, 50 MPa).

	Rates ratio $k_A/k_B$ (single products)	Reactivity ratio $R_{A/B}$ (competitive experiments)	$K_A/K_B$
DBT/4-MDBT	3.2	4	1.3
4-MDBT/4,6-DMDBT	1.9	2.5	1.3
DBT/4,6-DMDBT	6	8	1.3
DBT/2,8-DMDBT	0.45	0.53	1.2

From Ref. [30].

**Table 3**

Effect of methyl substitution in DBT skeleton on HDS activity of Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.

Mixture A	DBT	4-MDBT	4,6-DMDBT
Relative activity	1.00	0.43	0.17
Mixture B	DBT	2-MDBT	2,8-DMDBT
Relative activity	1.00	1.50	1.97

From Ref. [34] the molar ratio of DBT derivatives in mixtures A and B was 1/1/1.

be explained by different adsorption strengths at the catalyst surface.

Taking into account these results, an adsorption by the sulfur atom is unrealistic. The constants of adsorption would be otherwise greatly different for molecules sterically hindered by methyl groups around the sulfur atom. Following this conclusion, it could be assume a flat adsorption of the DBT and substituted DBT by the  $\pi$  electrons of the aromatic system as proposed by Singhal et al. [31]. That supposes a subsequent destabilization of the molecule, leading probably to a preliminary hydrogenation of at least one double bond, as represented in Fig. 2.

This dihydridobenzothiophene could then be further hydrogenated into tetrahydro- and hexahydro-dibenzothiophene or desulfurized by elimination to provide biphenyl. This last pathway has been proposed by Kasztelan to illustrate the HDS and HDN mechanisms [32]. Lower reactivities of 4-MDBT and 4,6-DMDBT could be therefore explained by a steric hindrance generated by the methyl groups for the basic attack (elimination reaction) and the higher reactivity of 2,8-DMDBT is explained by an easier and faster formation of the partially hydrogenated intermediate, due to the donor effect of the methyl group.

Such an approach was extended to the transformation of 4,6-dialkyldibenzothiophenes substituted with more voluminous alkyl groups and results obtained by Macaud et al. [27] are in complete agreement with the previous mechanism.

The same approach has been also used by Bataille et al. [33] for the transformation of DBT and 4,6-DMDBT in a continuous high pressure flow unit over CoMo and NiMo sulfided catalysts and their conclusions highly supported this work.

To also elucidate the influence of the position of the methyl groups on the conversion of DBT derivatives an elegant approach, unfortunately scarcely reported in the literature, has been developed few years ago by Saito and Segawa [34]. These authors investigated the HDS of a mixture of DBT, 4-MDBT and 4,6-DMDBT with a molar ratio of 1/1/1 and for comparison also tested a mixture of DBT, 2-MDBT and 2,8-DMDBT. The reactions were performed in a fixed bed high pressure flow reactor at 573 K and over a Mo/Al<sub>2</sub>O<sub>3</sub> catalyst.

Results reported in Table 3 for DBT, 4-MDBT and 4,6-DMDBT indicate that relative reactivities are exactly in the same order and with the same ratio than those obtained by Meille et al. [30] for independent experiments. Taking into account the 1/1/1 initial molar ratios of the 3 DBT derivatives, that could be only explained by an equal distribution of the 3 reactants over the catalytic sites which imply the same adsorption coefficient. These results also pointed out the positive effect of the methyl group in 2 or (and) 8 position, which has been correlated to an easier hydrogenation ability of the aromatic ring to get the partially hydrogenated intermediate.

Need of hydrogenation of an aromatic ring before carbon–sulfur bond rupture instead of direct hydrogenolysis, and positive effect of the alkyl group on the hydrogenation is however still discussed in the literature. However, that could be highly supported by a recent work of Kallinikos and coworkers [35] who compared the reactivities of refractory sulfur compounds present in a heavy gasoil. The real feed was hydrotreated with a commercial NiMo/γAl<sub>2</sub>O<sub>3</sub>

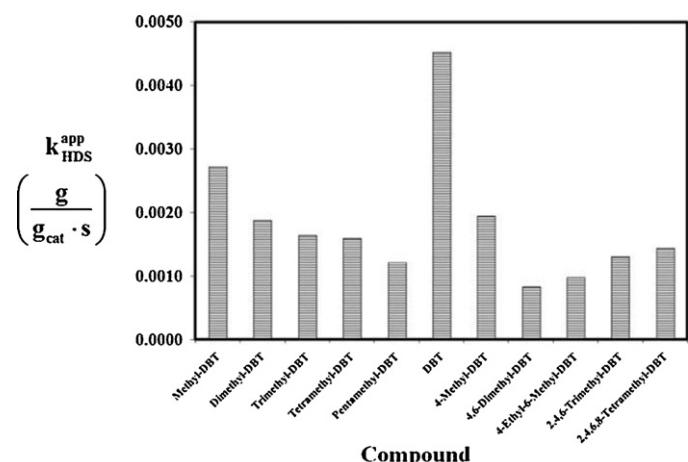


Fig. 3. Apparent reaction rate constants of DBTs, obtained at 613 K over a NiMo/γAl<sub>2</sub>O<sub>3</sub> catalyst.

From Ref. [35].

catalyst under commercial operation conditions of temperature. The results presented in Fig. 3 show that the most refractory sulfur compound is the 4,6-DMDBT, in agreement with the literature data. Moreover, these results also pointed out that more substituted compounds as 2,4,6-trimethylbenzothiophene and 2,4,6,8-tetramethylbenzothiophene are slightly less refractory, which could be related to the positive effect of the added methyl group on the hydrogenation of the aromatic ring, in agreement with the proposal of Meille et al. [30].

#### 4. Application of competitive kinetics for the understanding of the H<sub>2</sub>S inhibiting effect over transition metal sulfides (TMS)

In the field of heterogeneous catalysis, volcano curves play a key role to correlate catalytic activities with intrinsic properties of catalysts such as its ability to form chemical bonds with reactants, products or intermediates. For sulfide catalysts these periodic trends have been investigated from both experimental and theoretical sides [1,2,36] and from experiments most of the studies either in HDS, HDN or hydrogenation agreed with the statement that group VIII metal sulfides of the first row are poorly active whereas second and third rows are much more active. From these experimental observations, many attempts have been proposed to establish relationships between activity and intrinsic properties of the transition metal sulfides (TMS). One of the most recent approach using the metal sulfur bond energy  $E(M-S)$  descriptor in TMS gave a good interpretation of the volcano curve [37].

However, though H<sub>2</sub>S generally acts as an inhibitor on conventional systems based on Mo or W disulfides and unconventional sulfide active phases as Pd, Ru and Rh, Guernalec et al. [38] recently reported that H<sub>2</sub>S may also enhance the turnover rate in toluene hydrogenation with Co<sub>9</sub>S<sub>8</sub> and Cr<sub>2</sub>S<sub>3</sub> catalysts which present a low  $E(M-S)$ ; this effect is illustrated in Fig. 4.

Such a positive effect of H<sub>2</sub>S has been only theoretically considered in the past by Kasztelan and Guillaume [39] for toluene hydrogenation and by Olgun and Vrinat [40] for dibenzothiophene HDS on conventional Ni(Co)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. In their kinetic models these authors considered complex kinetic pathways including H<sub>2</sub> and H<sub>2</sub>S heterolytic dissociative activation on the catalytic sites.

Based on this model, kinetic equations for toluene hydrogenation have been established [41]. If the first addition of hydrogen

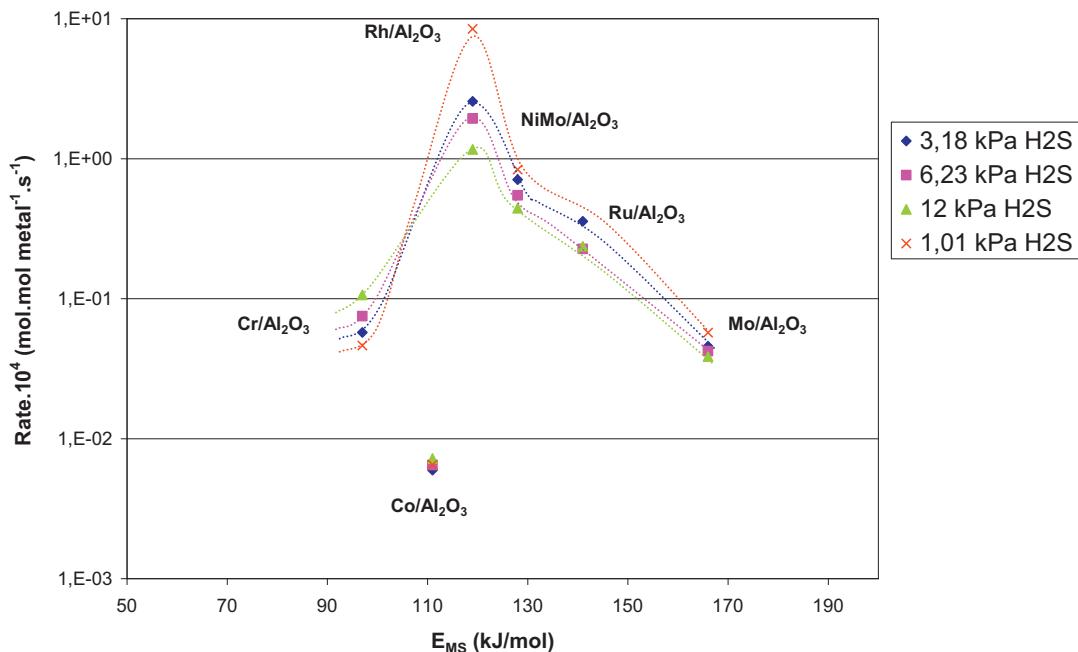


Fig. 4. Influence of  $\text{H}_2\text{S}$  partial pressure on toluene hydrogenation for several TMS.

From Ref. [38].

atom to the aromatic ring is a hydride like specie ( $\text{H}^{\delta-}$ ), as illustrated in Fig. 5a, and assuming that step to be the rate determining one, the rate equation is expressed as:

$$r = \frac{k_{\text{HYD}} C_0 K_R P_R K_{\text{H}_2} P_{\text{H}_2} (1 + K_R P_R)^{-0.5} (K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}} + K_{\text{H}_2} P_{\text{H}_2})^{-0.5}}{[(K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}})^{0.5} + (1 + K_R P_R)^{0.5}]^2} \quad (9)$$

in which  $K_i$  represents an adsorption equilibrium constant,  $P_i$  the partial pressure of the corresponding specie and  $C_0$  the total active sites concentration.

Taking into account the relatively high temperature of the reaction (623 K) and the low partial pressures of  $\text{H}_2\text{S}$  and toluene, we can consider  $1 \gg K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}} > K_R P_R > K_{\text{H}_2} P_{\text{H}_2}$ . Therefore, the order relative to  $\text{H}_2\text{S}$  is  $-0.5$ , which could explain the results observed for TMS with high  $E(\text{M-S})$ .

On the contrary, if the first addition of hydrogen atom to the aromatic ring is a proton like specie ( $\text{H}^{\delta+}$ ), as illustrated in Fig. 5b, and assuming that step to be rate determining, the rate equation is expressed as:

$$r = \frac{k_{\text{HYD}} C_0 K_R P_R (K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}})^{0.5}}{(1 + K_R P_R)^{0.5} [(K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}})^{0.5} + (1 + K_R P_R)^{0.5}]^2} \quad (10)$$

Assuming also  $1 \gg K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}} > K_R P_R > K_{\text{H}_2} P_{\text{H}_2}$ , the order relative to  $\text{H}_2\text{S}$  is  $+0.5$ , which could explain the results observed for TMS with low  $E(\text{M-S})$  such as  $\text{Cr}_2\text{S}_3$  and  $\text{Co}_9\text{S}_8$ .

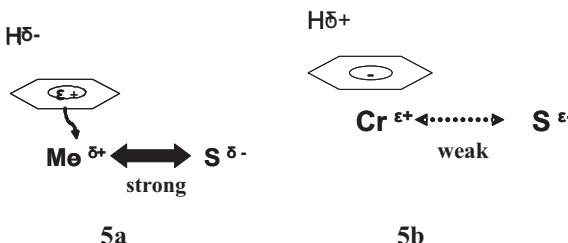


Fig. 5. Adsorption models for high and low  $E(\text{M-S})$  sulfides.

Variations of such reaction order relative to the  $\text{H}_2\text{S}$  partial pressure could be therefore attributed to differences in the electronic properties of the corresponding sulfides. In order to check such variations Guernalec [41] used the competitive hydrogenation between benzene and toluene. This approach has been elegantly used in the past by Tri et al. [42] to evidence the changes in electronic properties of Pt over various supports. Indeed, due to the presence of the methyl group in the toluene molecule, a high ratio  $K_T/K_B$  was associated to an electron deficient character of the metallic site.

Concerning the transition metal sulfide catalysts, it can be observed in Table 4 that over cobalt and chromium sulfides which present low  $E(\text{M-S})$ , toluene is more strongly adsorbed than benzene, though it is the contrary over sulfides having a higher  $E(\text{M-S})$ . These results clearly support the proposal of variations in the electronic state of the catalytic sites with the nature of the sulfide, and once again demonstrate the interest of this kinetic approach in the comprehension of the catalysts.

## 5. Understanding support effect for $\text{ReS}_2/\text{Al}_2\text{O}_3$ and $\text{ReS}_2/\text{SiO}_2$ catalysts

The support effect had focussed a great interest of numerous studies in hydrotreating catalysts. For example, it has been well demonstrated that the support was not only a carrier for dispersing the active phase, but could also introduce very interesting properties concerning the structure of the active phase, or

Table 4  
results of independent and competitive experiments, for benzene or (and) toluene hydrogenation.

Catalysts	$k_T$	$k_B$	$k_T/k_B$	$R_{B/T}$	$K_B/K_T$
$\text{Cr}_2\text{S}_3$	$6.6 \times 10^{-8}$	$1.2 \times 10^{-8}$	5.5	0.08	0.44
$\text{Co}_9\text{S}_8$	$1.1 \times 10^{-8}$	$1.2 \times 10^{-8}$	0.9	0.15	0.14
$\text{NiMoS}/\text{Al}_2\text{O}_3$	$3.8 \times 10^{-7}$	$1.5 \times 10^{-7}$	2.5	0.58	1.44
$\text{RuS}_2$	$5.9 \times 10^{-6}$	$2.5 \times 10^{-6}$	2.3	0.81	1.90
$\text{MoS}_2$	$8.4 \times 10^{-8}$	$1.4 \times 10^{-8}$	6.0	0.22	1.31

From [41].

**Table 5**

Catalytic activities of  $\text{ReS}_2/\text{Al}_2\text{O}_3$ ,  $\text{ReS}_2/\text{SiO}_2$  and  $\text{NiMo}/\text{Al}_2\text{O}_3$  catalysts, in single and competitive reactions for benzene and toluene hydrogenation.

Catalyst	Rate single experiments ( $10^{-8} \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1}$ )		Rate competitive experiments ( $10^{-8} \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1}$ )		$k_B/k_T$	$R_{B/T}$	$K_B/K_T$
	$k_B$	$k_T$	$k_B$	$k_T$			
$\text{ReS}_2/\text{Al}_2\text{O}_3$	13	11	8.7	5.3	1.2	2.5	2.1
$\text{ReS}_2/\text{SiO}_2$	16	13	2.4	6.8	1.2	1.8	1.5
$\text{NiMo}/\text{Al}_2\text{O}_3$	13	18					

bi-functionality, which could drastically improve the catalytic activity [9–11]. Such effects have been mainly reported for molybdenum disulfide based catalysts, using alumina, titania and zirconia supports, but the interpretations are sometimes contradictory with a balance between electronic and geometrical effects. However, non-conventional supports such as  $\text{TiO}_2$  and  $\text{ZrO}_2$  are still considered as promising for  $\text{MoS}_2$  supported catalysts.

In a recent paper, Laurenti et al. [43] found that the catalytic activity of rhenium sulfide in thiophene hydrodesulfurization was also deeply dependant of the nature of the support, but contrary to supported  $\text{MoS}_2$  catalysts, titania-supported  $\text{ReS}_2$  was observed to be less active than  $\text{ReS}_2/\text{Al}_2\text{O}_3$ . Moreover, Sepulveda et al. [44] reported a very high level of conversion on a  $\text{ReS}_2/\text{SiO}_2$  catalyst in HDS of 4,6-dimethylbenzothiophene as compared to  $\text{ReS}_2/\text{Al}_2\text{O}_3$  (see Fig. 6), such an activity being 6 times higher than the one observed for the industrial  $\text{NiMoS}/\text{Al}_2\text{O}_3$  reference. These variations of activities between  $\text{ReS}_2/\text{SiO}_2$  and  $\text{ReS}_2/\text{Al}_2\text{O}_3$  have been confirmed at different loadings of rhenium, suggesting that the catalytic activities variations were really due to some specific support effect.

Taking into account that the variations observed in 4,6-DMDBT have been found more pronounced than those determined during the HDS of thiophene [44], the authors proposed to reexamine their results in relation to the mechanism of transformation of both molecules. Indeed, for thiophene HDS, the C–S bond rupture can be realized directly to give butadiene which is further hydrogenated, or the C–S bond cleavage can follow C–C double bond hydrogenation [45], though for 4,6-DMDBT hydrodesulfurization the C–S bond cleavage has been proposed to be mainly the result of an  $E_2$  elimination reaction following a partial aromatic ring hydrogenation [30,33]. Such observations suggested differences coming from the aromatic ring hydrogenation step and therefore from a “metallic like character” of these sulfides. In order to support such a hypothesis, the authors proposed to compare the catalysts toward the hydrogenation of benzene and toluene first in separated experiments and later in competitive experiments.

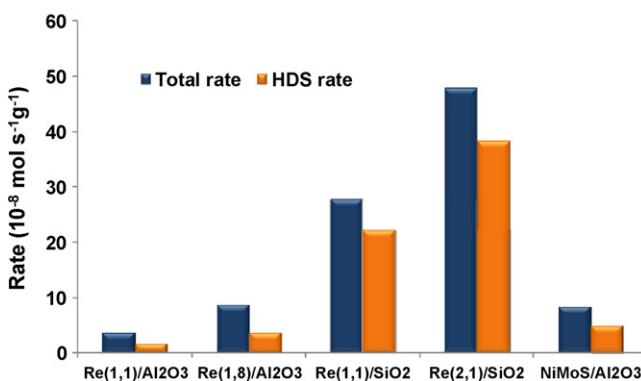


Fig. 6. Specific rates of HDS and of total conversion for the transformation of 4,6-DMDBT at 573 K over various rhenium sulfide supported catalysts.

From Ref. [44].

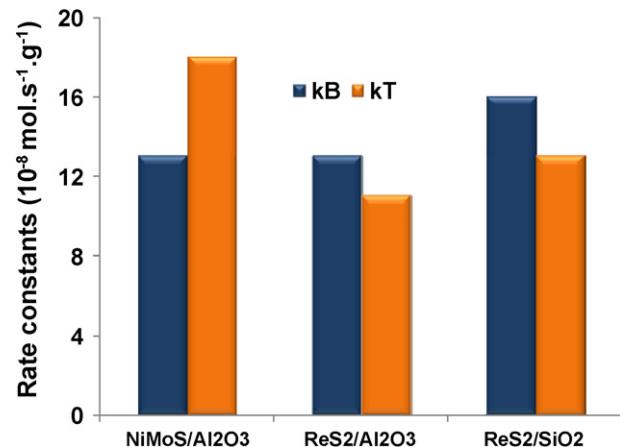


Fig. 7. Rate constants for toluene ( $k_T$ ) and benzene ( $k_B$ ) hydrogenation in independent experiments.

From Ref. [44].

For independent experiments, the results given in Fig. 7 indicate that  $k_T < k_B$  for both rhenium sulfide supported catalysts, though the reverse is observed for the NiMoS supported sample. Such inversion between  $k_B$  and  $k_T$  has been previously reported in the literature. Indeed, for  $\text{WS}_2$  and  $\text{NiMoS}$  sulfide catalysts, the rate of toluene hydrogenation was found to be higher than that of benzene [41,46]. In contrast, for metal catalysts, the rate of hydrogenation of substituted benzene is still lower than that of benzene, according to the well known Lozovoy formula [47]. Such results support the previous proposal of a “metallic like character” for the supported rhenium sulfide catalysts.

In order to complete these observations, difference in the “metallic like character” between  $\text{ReS}_2/\text{SiO}_2$  and  $\text{ReS}_2/\text{Al}_2\text{O}_3$  has been checked by the technique of competitive kinetics between benzene and toluene (see Section 4). Results reported in Table 5 indicate a lower  $K_B/K_T$  ratio over  $\text{ReS}_2/\text{SiO}_2$  than over  $\text{ReS}_2/\text{Al}_2\text{O}_3$  suggesting again a higher metallic character of the  $\text{ReS}_2$  active phase over  $\text{SiO}_2$  than over the  $\text{Al}_2\text{O}_3$  support.

Rhenium sulfide based catalysts have been found similar to ruthenium sulfide catalysts regarding the influence of the sulfidation mixture [48], and for ruthenium sulfide supported over zeolite, using HREM, EDX, TPR, and EXAFS, Morawec et al. [49] demonstrate that the active phase consists of clusters of ruthenium sulfide-like phase with small domains of ruthenium metal. Therefore existence of this metallic like-character for  $\text{ReS}_2$  based catalysts is not surprising, and contributes to understand this unexpected support effect.

## 6. Conclusion

Kinetics has been early used by the process engineers to develop, for a specific reaction, a mathematical model able to predict the effects of reactor operating changes on performance, and therefore permits any extrapolation, optimization and control of an industrial

process. However, the kinetics of a reaction is directly associated to its mechanism and use of a reaction as a probe for understanding the surface is probably one of the best *in situ* technique. That could be done by various kinetic approaches here illustrated with competitive experiments related to the understanding of deep desulfurization of diesel, to the comprehension of transition metal sulfides and the support effect for sulfide catalysts. All these results illustrate how such an approach could be rich in conclusions.

The authors hopes that lecture of this paper will convince young researchers to never forget this part of the investigation.

## Acknowledgments

M.V. would like to thank the editors to invite him to participate to this special issue.

It allows him the opportunity to thank Jean Marie Herrmann for his important contribution to the field of catalysis and for more than 40 years of long standing professional and personal friendship. Thank also to J.M. H. to believe in the kinetic approach to understand catalysis.

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